

COLORFAST DYES FOR WASHABLE AND DRYCLEANABLE LEATHERS. VINYL SULFONE REACTIVE DYES

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ABSTRACT

Vinyl sulfone reactive dyes were tested on glutaraldehyde- and chrome-glutaraldehyde-tanned leather. These leathers withstood the high pH requirements of the vinyl sulfone dyeing procedure, and yielded products with level color and excellent color penetration. Experimental work showed that the excellent colorfastness properties of these dyes in leather were added to the washable and perspiration-resistant qualities of glutaraldehyde tannages. These dyes are applicable to grain and suede leathers and need not be limited to use on oil-tanned chamois skins.



INTRODUCTION

The stability and resistance of glutaraldehyde- and glutaraldehyde-chrome-tanned leathers to the effects of washing in soap and water, and the need for washfast dyes for use on these leathers, have been described (1-4). Mullen reported (5, 6) that Procion M†† reactive dyes, based on the reactive chlorine of the cyanuric chloride moiety of these dyes, were colorfast upon reaction with chrome-tanned leather. We found those dyes to be even better when applied to glutaraldehyde- and chrome-glutaraldehyde-tanned leathers (7).

Vinyl sulfone dyes (Remazol** reactive dyes) were reported recently (8, 9) to give colorfast, washable, and drycleanable oil-tanned chamois leathers. Chamois was used because it was able to withstand the high pH of 9 to 10 necessary for the dyeing procedure. We now have tested these reactive dyes on glutaraldehyde- and chrome-glutaraldehyde-tanned leathers which also withstand such reaction conditions. The results have been very satisfactory.

The chemistry of reactive dyes has expanded greatly in the last eight years—from three dyes in 1965 to many hundreds at present. A comprehensive treatment

*Agricultural Research Service, U. S. Department of Agriculture.

†Trade name—Imperial Chemical Industries (ICI).

‡Reference to brand or firm does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

**Trade name—American Hoechst Corp.

the subject is now available (10). It would appear at this time, however, that any of these dyes could not be used for leather.

EXPERIMENTAL

The experimental procedure was similar to that described by Rosenbusch and Abbott (8) and by Seyd (9). Minor changes were made for convenience or cause of improved results with the leather under experimental treatment. Most of the work was done with a commercial glutaraldehyde-tanned leather that was made into a light-weight garment leather. This leather was dry and completely processed for commercial use, and was used, as received, in the dyeing procedure described below.

Dyeing Procedure

All percentages listed in *Steps (a), (b), and (d)*, are based on the dry weight of the leather.

Step (a) One skin (or half skin) was wet back in 1000 percent water containing two percent concentrated ammonium hydroxide (29 percent NH_3) and 0.5 percent Triton GR5†† for $\frac{3}{4}$ hour, starting with water at 50°C. (122°F.). Agitation was supplied by the back-and-forth action in a washing machine. The skin was then well rinsed in sufficient changes of water to remove ammonia. Water squeezed from the skin at this time was in the pH range of 7 to 7.5.

Step (b) The skin was drained, or hand squeezed, and then dyed with the even Remazol dye as follows. The skin was tumbled about five minutes in an alkaline solution made up of 300 percent water and ten percent sodium carbonate monohydrate (proportional amounts of soda ash may be used). Then one to five percent dye was added, preferably to the float and not onto the skin. Tumbling was continued for about two hours at 50°C. (122°F.) with the pH very close to 10. Heat lamps were used to preheat the small fiber-glass-plastic drum and to maintain the temperature at 50°C.

Step (c) The skin then was rinsed, usually with several batch rinses (about five minutes each) in the washing machine. To assure the removal of residual, reacted dye, the skin then was washed in soapy water (approximately 25 grams of white soap flakes in about 30 liters of water) in the washing machine for 30 minutes at 50°C. (122°F.). The skin then was rinsed with vigorous agitation in several changes of water to remove the soap.

Step (d) The skin was acidified by treating in 500 percent water containing 5 percent formic acid (90 percent grade) for 45 minutes, and then rinsed until the pH of the water squeezed from it was 3.8 to 4.0. The skin then was ready for refatliquoring to achieve the softness desired in the finished leather.

In addition, other glutaraldehyde-tanned sheepskins, as well as chrome-glutaraldehyde-tanned grain-garment sheepskins and straight chrome-tanned garment

††Trade name—Rohm & Haas wetting (and rewetting) agent.

sheepskins, were dyed, using a procedure essentially similar to the one described above. These skins were dyed immediately after tanning, with no intermediate fatliquoring, drying ("crusting" or "stain sorting"), or finishing stage. The skins were fatliquored and processed after they were dyed.

Wash Tests

The wash tests were done according to the ASTM-ALCA procedure (11), wherein the specimens are washed under specified conditions in 0.5 percent soap solution for 0.5 hour at 50°C. (122°F.). Each test series consisted of four leather pieces: one unwashed, one washed once, a third washed twice, and the fourth washed three times. All the specimen pieces were air-dried overnight between washes. A fresh multifiber test cloth (12) was included in each wash cycle to detect staining. Each test fiber was present as a $\frac{1}{4}$ - to $\frac{3}{8}$ -inch strip on the test cloth made up of wool, viscose rayon, spun silk, nylon, bleached cotton, and acetate with a warp yarn of Dacron.

Drycleaning Tests

The drycleaning tests on the dyed leather specimens were intended primarily to check for color-run from the leather, as indicated by color change of the drycleaning solvent and/or staining of the test fabric. The test was run by using the equipment and procedure indicated for the wash tests with 50 ml. of drycleaning solvent at room temperature in place of the hot soap solution. A separate set of dyed leather pieces (each color) was tested in each of the three most common drycleaning agents: Stoddard Solvent, perchloroethylene, and Valene††.

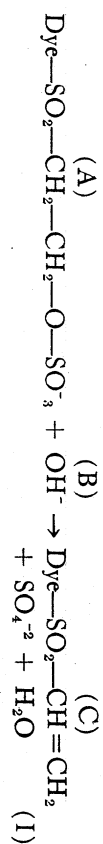
DISCUSSION AND RESULTS

The first reactive dyes reported for use with leather were based on cyanuric chloride, wherein two chlorine atoms were available as reactive sites, *i.e.*, Procion M type dyes (5-7, 14). These dyes reacted readily at temperatures low enough for most leathers. Recently (1968-1970) there have been several papers published concerning the reaction of vinyl sulfone reactive dyes (Remazol type) with collagen films (13) and with chamois leather (8, 9), at suitable temperatures. These reports indicated that this reaction was suitable only for leathers that withstand treatment at pH values near 10. Presumably, these dyes could not be used on standard chrome-tanned leathers that usually are tanned and fatliquored at pH values below 6. However, we have found chrome-glutaraldehyde- and glutaraldehyde-tanned leathers (washable leathers) (1-4) are suitable for dyeing with the vinyl sulfone dyes, because they are resistant to high pH.

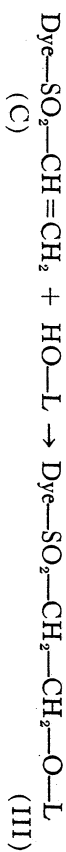
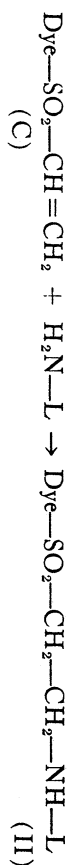
Although the chemical reactions between vinyl sulfone dyes (Remazol) and leather differ from those of the cyanuric chloride-type dyes (Procion M), both dyes are simple to use. The vinyl sulfone dye-leather reaction has been described

††Trade name—DuPont (1,1,2-trichloro-1,2,2-trifluoroethane).

(8, 9, 13), but is outlined below for the convenience of those who do not have the references. Essentially, the overall reactions may be described as follows. The dye, as introduced into the bath containing the leather, is in a "masked" reactive form (A). The reactive vinyl group (C) is formed under the influence of the alkali (sodium carbonate or soda ash) (B) added during the dyeing procedure (Reaction I):

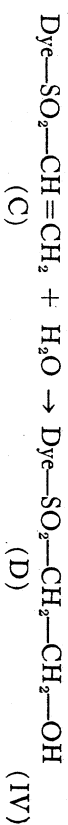


The vinyl group reacts readily with the active hydrogen of primary and secondary amino groups and of alcoholic groups present in the leather (L) (Reactions II and III):



The reactions II and III above form covalent bonds that make the dye become part of the leather molecule and therefore quite resistant to washing or drying. In glutaraldehyde-treated leathers, many of the amino groups already have reacted with the aldehyde. This enhances dye penetration and level surface color.

The soluble color, which must be washed out of the leather immediately after the dye treatment, is mostly excess dye solution containing, also, a hydrated product (D) formed to some extent during the dye treatment (Reaction IV):



At this time, thorough rinsing and washing with soap and water are required to remove all soluble color.

Eleven dye colors, selected at random from the many available, were used on the leathers described under "Experimental." At dye concentrations of one, two, three, and five percent, based on the dry weight of the leather, the dyed leather was of level color on the desired ("sueded") side of the glutaraldehyde-tanned leather (Table II). On higher quality grain leathers, with or without chrome, a series of experiments gave level colors on both the grain and flesh sides, using three and five percent dye. Table III lists results for chrome-glutaraldehyde-tanned leathers treated with five percent vinyl sulfone dyes. We were not able to get equally level color with five percent (same basis) on oil-tanned chamois made to U.S. Government specifications by a leading chamois tanner. Apparently,

the glutaraldehyde-treated skins were easier to color well, without any special effort or "know-how," than oil-tanned chamois. In all experiments with sheepskins, the dye penetrated the entire thickness of the skins. For most of the dyes used in these experiments, depth of color differed little among the two- to five-percent dye treatments. Leathers dyed with equal amounts of dye for only one hour did not develop as deep a color as similar leathers treated for two hours.

Leather Stability

The versatility of glutaraldehyde as a tanning agent, and the properties it imparts to leather, are well known (1-4, 15-22). Colored leathers quite similar to chamois can be made if desired, but grain and suede garment and glove leathers also can be made. These leathers have shrink temperatures that are much higher than that of oil-tanned chamois and the leathers are of wider, general use. These leathers, properly tanned or retanned with glutaraldehyde, will retain the ability to withstand high pH, not only through the dye treatment with vinyl sulfone dyes, but through many soap and water wash cycles afterward. Table I shows data on the stability of the leather, as differentiated from stability of color, after

TABLE I

STABILITY* OF VINYL SULFONE-DYED LEATHERS TO WASHING

Leather and Tannage	Wash Cycle	Shrink Temperature (°C.) of Dyed Leather				
		Yellow GR	Brilliant Blue R	Red B	Green 5 GA	Dark Brown
Glutaraldehyde-tanned† domestic sheepskin, T _s = 80°C.	0	78		78	79	77
	1	77		77	78	76
	2	77		77	77	76
	3	76		76	77	75
Chrome-glutaraldehyde† combination-tanned Nigerian sheepskin, T _s = 97°C.	0	89		90		
	1	88		89		
	2	87		88		
	3	87		87		
chromium (Cr ₂ O ₃) = 3.52%‡						
Chrome-tanned Nigerian sheepskin, T _s = 98°C.	0	89		90	89	90
	1	86		85	85	85
	2	79		80	80	80
chromium (Cr ₂ O ₃) = 2.96%‡	3	78		79	78	79

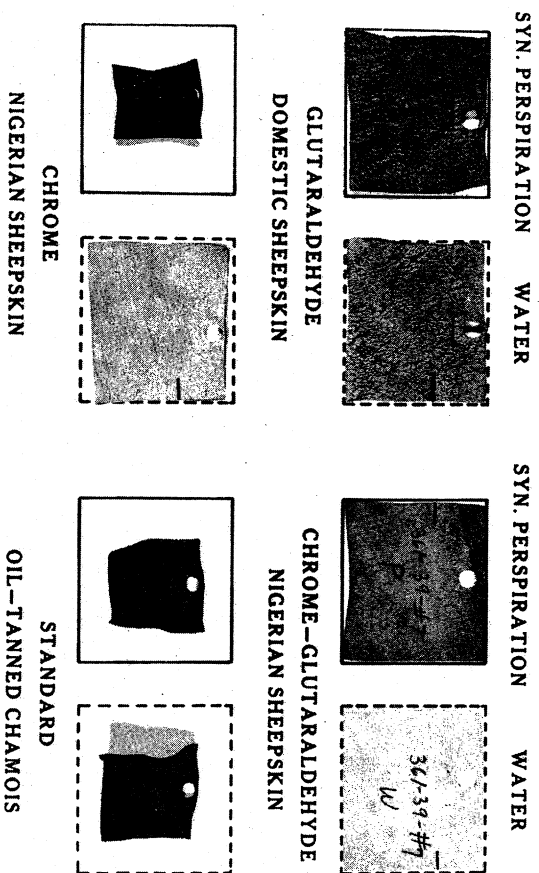
*This table is concerned with stability of the leather *per se* after two-hour dye treatment at pH 10, as differentiated from color stability (fastness) shown in Tables II and III. Remazol® Fiber Reactive Dyes were used.

†Amount glutaraldehyde used—ten percent of the 25 percent commercial solution based on the pickled or blue weight of skins.

‡Determined by atomic absorption spectroscopy (see Ref. 25).

the dye treatment. The shrink temperature of the glutaraldehyde-tanned leather dropped from 80°C. to 75-77°C. after the two-hour dye treatment (pH 10) and three ½-hour wash cycles in soap and water (pH ca. 10) at 50°C. The shrink temperature of chrome-glutaraldehyde combination-tanned garment leather dropped from 97°C. to 87°C. after the same treatment. The shrink temperature of the same chrome-tanned garment leather, without the glutaraldehyde retannage, dropped from 98°C. to 78°C. after similar treatment. These data support results from previous work (3) on low-chrome Cabretta glove leathers wherein the shrinkage temperature of undyed chrome-tanned leather dropped 29°C. (from 87 to 58°C.) after three wash cycles. In that same test, the shrinkage temperature of chrome-glutaraldehyde-tanned glove leather dropped only 10°C. and straight glutaraldehyde-tanned leather showed essentially no change.

SYNTHETIC PERSPIRATION TEST



TREATED: Vinylsulfone dyes - 2 hrs. - pH 10

FIGURE 1.—Effect of ASTM-ALCA perspiration test (D2322-69) on vinyl sulfone-dyed leathers. Duplicate test using water in place of test-solution is shown for comparison.

In addition, the leather is resistant to the effects of perspiration. Figure 1 shows that glutaraldehyde-tanned leather and chrome-glutaraldehyde-tanned leathers retain the property of resistance to the standard synthetic perspiration test (1, 23, 24) after the high pH dye treatment. Straight chrome-tanned leather and oil-tanned chamois did not pass the test.

Color Stability

The results of wash tests (11, 12) on dyed leather samples are shown in Tables II and III. Table II, concerned with glutaraldehyde-tanned leather,

TABLE II

WASH FASTNESS OF GLUTARALDEHYDE-TANNED SHEEPSKIN LEATHER DYED WITH VINYL SULFONE DYES*

"Remazol" Dye**	Color Changes Due to Wash Test† — Gray-Scale Rating							
	Transfer to Test-Cloth Segment							
	Dyed†† Leather	Spun Acetate	Bleached Cotton	Spun Nylon 66	Spun Silk	Spun Viscose	Wool (Worsted)	
Brown GR	(2) 5 (3) 4-5 (5) 4-5(4)	5 5 5	4-5 4-5 3	5 5 5	5 5 3	4-5 4-5 5	5 5 5	
Green 5GA	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
Red B	(2) 5(4-5) (3) 5(4-5) (5) 5(4-5)	5 5 5	4-5 4 4	4-5 4 4	5 4-5 4-5	5 5 4-5	5 5 5	
Yellow GR	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
Brilliant Blue R	(2) 4-5 (3) 4-5 (5) 4-5	5 5 5	5 5 5	4-5 3-4 3-4	4 3 3	5 5 5	5 5 5	
Gray G	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
"Black" B	(2) 5(4-5) (3) 5(4-5) (5) 5(4-5)	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
Brown 3G	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
Dk. Brown R	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
Violet 5R	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	
Blue 3R	(2) 5 (3) 5 (5) 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	5 5 5	

*Remazol® Fiber Reactive Dyes, American Hoechst Corp., Somerville, N. J. 08876.

†ASTM (ALCA) Designation: D 2096-69 (see Ref. 11). (Value 5 = essentially no color change or staining).

††Multifiber fabric #1 (see Ref. 12).

**Number in parentheses = percent dye based on dry weight of skin.

†††Gray scale rating for 1st wash cycle; rating for two subsequent wash cycles in parentheses, if there is a change.

TABLE III WASH FASTNESS OF CHROME-GLUTARALDEHYDE LEATHER* DYED WITH VINYL SULFONE DYE†

"Remazol" Dye††	Color Changes Due to Wash Test — Gray Scale Rating					
	Transfer to Test-Cloth** Segment					
	Dyed‡‡ Leather	Spun Acetate	Bleached Cotton	Spun Nylon 66	Spun Silk	Spun Viscose (Wor- sted)
Yellow GR	5	5	5	5	5	5
Gray G	5	5	5	5	5	5
Brown GR	5(4-5)	5	4	5	4	4-5
Green 5GA	5	5	5	5	5	5
"Black" B	5	5	5	5	5	5
Red B	5(4-5)	5	4	4	4	4-5
Brilliant Blue R	4-5	5	5	3-4	3	5

*Nigerian hair-sleep skins (glove and garment weight); Cr (as Cr₂O₃) = 3.52% (determined by atomic absorption spectroscopy—see Ref. 25).

†Remazol® Fiber Reactive Dyes, American Hoechst Corp., Somerville, N. J. 08876.

‡ASTM (ALCA) Designation: D 2096-69 (see Ref. 11). (Value 5 = essentially no color change or staining).

**Multifiber Fabric #1 (see Ref. 12).

††Five percent dye based on dry weight of leather.

‡‡Gray scale rating for 1st wash cycle; rating for two subsequent wash cycles in parentheses, if there is a change.

includes data for three dye concentrations (two, three, and five percent). The ratings of 4-5 and 5 indicate that very little or no color was lost by washed specimens of leather. Fabric staining during the wash test was apparent only in a few cases. This was true even though there was always a little color in the soapy water, due, probably, to the rigor of the test conditions. Table III shows washfast data for chrome-glutaraldehyde leather dyed with five percent dye concentrations (see Experimental). Here, again, color loss by the leather specimens and staining of test fabrics were minimal. The data of both Tables indicate that the dye was quite fast when applied properly to the leathers listed above. Results of the drycleaning tests described under Experimental indicated no color-run into any of the solvents used. Slight changes in shade of treated samples were due to "cleaning" of the sample and to loss of fatliquor (fiber lubricant) to the solvent, and to some changes in nap texture.

In summary, the work reported here indicates that the use of vinyl sulfone dyes need not be limited to oil-tanned chamois leather. Apparently, they can be put to good use on leathers such as those described in this report.

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